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Nanoparticles: balancing benefits, ecological risks, and remediation approaches

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Abstract

Nanoparticles are the simplest form of structure, having sizes ranging from 1 to 100 nm and can provide considerably high surface areas through rational design. Their size, shape and structure are responsible for their high reactivity and strength. In the last few decades, nanoparticles have been widely used in many dosage forms due to their excellent solubility, less size and better penetrability. They have attained prominence in various technological advancements because their properties can be tuned as desired *via* precisely controlling the size, shape, synthesis conditions, and appropriate functionalization. Due to these unique properties, Nanoparticles have acquired a substantial global market in various commercial and domestic applications, including catalysis, imaging, medical applications, sports equipment, sensors, energy-based research, and environmental applications. Due to the increased growth of the production of nanoparticles and their industrial applications, issues relating to toxicity are inevitable. Several reports are available on the benefits of these nanomaterials in various sectors, but relatively more minor literature is available on their effect on the environment and human health. Several heavy metal nanoparticles are reported to be so rigid and stable that their degradation is not readily achievable, leading to much environmental toxicity. This review discusses a brief history, various applications and the possible fate of the Nanoparticles after use. In particular, we describe how Nanoparticles affect the environment, natural resources, natural micro-flora and humankind. It also describes several techniques currently being used to remove nanoparticles.

Keywords Nanoparticles, top-down, bottom-up, toxicity, life cycle impact assessment

1. Introduction

The concept of manipulating matter on an atomic level was seeded in 1959 when the great physicist Richard Feynman presented a lecture at the American Physical Society meeting at Caltech entitled “there’s plenty of room at the bottom” [1]. Since then, there have been revolutionary developments in nanotechnology. The fact that size can influence the physico-chemical properties of materials has led to significant discoveries worldwide by producing nanoparticles (NPs) with varied applications [2, 3]. According to a market study published by Global industry analyst Inc., entitled “Nanomaterial- Global market Trajectory & Analytics,” research and eventually production of the nanomaterials have grown exponentially in the last decade. According to the Global Industry Analysts, Inc [4], the global metal market size for nanomaterials is estimated at $US 7.9 billion in 2022, and it will reach a size of US $12.1 Billion by 2026, growing at a CAGR (Compound Annual Growth Rate) of 9.7% over the period. Global competitors in the field of nanotechnology cover over 233 companies, including Evonik Industries AG, Ahlstrom-Munksjö, American Elements, Altair Nanotechnologies Inc, Arkema Group, Covestro AG, Cytodiagnostics Inc, DuPont de Nemours Inc, Frontier Carbon Corporation, Hyperion Catalysis International Inc, and others [4].The reasons for this rapid growth in the field of nanoparticles are attributed to its varied properties and diverse applications. NPs find roles in every possible industry ranging from electronics, optics, healthcare and imaging, sports equipment, sensors, and energy-storage devices [5-7].

Although the benefits of these nanomaterials in various sectors have been well reported, the unprecedented use of these particles in either development or application may have a profound effect on the environment and human health, which is yet not fully understood. The different synthesis methods, an assembly involving harmful chemicals and massive energy, and material input produce different pollutants that possibly lead to different toxicological impacts. To date, most of the research has primarily focussed on the unique attributes of the nanomaterials in varied fields without considering the potential environmental impacts. In this review, we have briefly discussed both sides of the coin regarding the benefits of the nanomaterials and the risks/challenges they pose on the environment as a whole.

This systematic review summarizes the latest information on the properties, synthesis, and applications of NPs. We collect and discuss the current literature on their accumulation, toxicity, and the impact of environmental conditions. Finally, we summarize the ideas suggested by various researchers regarding removal techniques and outline potential future research directions and emerging trends in nanoparticle science.

2. Properties of the nanoparticles

Nanoparticles can be defined as the particles with at least one dimension having size less than 100nm. However, size can be varying depending on their different preparation methods. Nanoparticles can be present either in crystalline or in amorphous form [8] Some surprising properties of the nanoparticles make them different from bulk materials and change their mechanical, optical and electrical behavior.

The properties of the nanomaterials are uniquely distinct compared to the bulk materials because the size-dependent features become more prominent, which in turn dictates the nanomaterial's mechanical, optical and electrical behavior.

2.1 High surface area to volume (S/V) ratio

Nanoparticles have a large surface area per unit mass than micro-particles. For instance, the surface-to-volume ratio of a particle of size 60 nm is 1000 times higher than that of a particle of size 60 μm [8]. The surface area to volume ratio increases dramatically when the nanoparticle's diameter drops from 100 to 1 nm. This leads to an increase in the percentage of the atoms at the surface, making surface forces more dominant. Due to the high S/V ratio, the nanoparticles exhibit enhanced diffusion at elevated temperatures. This property of nanoparticles allows sintering to take place at lower temperatures than in the case of larger particles.

2.2 Thermal properties

Heat transfer in nanoparticles primarily depends on energy conduction due to electrons and photon vibration. The size of the NP material plays a direct role in its thermal conductivity. For example, graphene derived from graphite displays excellent thermal properties and heat transfer and is used in various applications. The high surface-to-volume ratio in NPs provides more electrons for heat transfer compared to the bulk materials. Also, micro convection from the Brownian movement in NP plays a key role in guiding its thermal properties (observed in the case of nanofluids). Due to low S/V, atoms at the surface have fewer atoms around; the binding energy also decreases with a decrease in the size of the particle. Hence, a reduction in the binding energy per atom also results in the reduction of melting point.

2.3 Optical effects

Nanoparticles are in the size regime where the fraction of light that is scattered or absorbed can vary greatly depending on the particle diameter. At diameters, less than 20 nm, nearly all of the extinction is due to absorption. At sizes above 100 nm, the extinction is primarily due to scattering. The optimal amount of scattering and absorption can be achieved by designing a particle with a larger or smaller diameter. Another by-product of this relationship between size and absorption/scattering is that aggregation can increase a nanoparticle's effective size, increasing scattering. This is why 20 nm diameter silica particles are transparent in solution, but re-suspensions of dried 20 nm silica particles (aggregated) will be a milky white colour.

Also, nanoparticles such as gold, silver etc., support Plasmon resonance where the wavelength of the incident beam matches the oscillating frequency of the nanoparticle. By tuning the size and shape, the peak resonance wavelength can be shifted across the visible and into the spectrum's infrared region, allowing for a wide range of colour tunability. For instance, silver nanoparticles between 10 and 50 nm have a characteristic brown color due to the Surface Plasmon Resonance effect [9].

2.4 Magnetic features

Nanomaterials possess superparamagnetic properties. They exhibit high magnetization when exposed to a strong magnetic field, and the magnetization property vanishes on removal of the field. Small NPs possess single magnetic domain structures below a certain critical radius (r_c), where all magnetic spins in the NP align unidirectionally. However, the NP radius has to be lower than the threshold radius for superparamagnetism (r_{sp}) to be superparamagnetic.

2.5 Mechanical properties

Mechanical properties of nanomaterials may reach the theoretical strength, which is one or two orders of magnitude higher than that of single crystals in the bulk form. The enhancement in mechanical strength is simply due to the reduced probability of defects. Due to this fact, nanoparticles can sustain extremely high stresses (in the GPa range) and ductility, even in the case of brittle materials [10].

3. Nanoparticle synthesis

3.1 Microstructural properties of $SnSb_2S_5$ thin films

Nanoparticles can be synthesized using top-down and bottom-up approaches (Figure 1). The top-down synthesis is a destructive method involving decomposing larger molecules from the bulk material into a smaller molecule that later transforms into nanoparticles [11]. The top-down synthesis mainly comprises grinding/milling, physical vapour deposition, electrospinning, etc., and other decomposition techniques [12]. On the other hand, the bottom up (BU) approach involves relatively simpler substances, also termed as the "building up" approach. It refers to the build-up of material from the bottom: atom-by-atom, molecule-by-molecule, or cluster-by-cluster [13]. The method creates less waste and is more economical than the "top-down" method. Moreover, the BU approach has many merits, such as fewer defects, more homogenous chemical composition, and better ordering. Chemical vapour deposition, reverse-micelle route, sol-gel synthesis, hydrothermal synthesis, etc., are some well-known bottom-up techniques employed in nanoparticle synthesis. Table 1 highlights a brief of these methods with their different applications.

3.2 Green synthesis

Both the top down and bottom up approaches involve physical or chemical nanoparticle synthesis methods, which have certain drawbacks. The physical methods require significant time to achieve thermal stability, consume a lot of input energy, and contribute greatly to global warming. The chemical methods, on the other hand, employ harsh chemical reagents. Alternatively, biological synthesis has been envisaged by researchers as a more benign route with very less environmental impacts. The biological or green synthesis employs different micro-organisms such as bacteria, fungi, yeast and plant extracts [14]. Microbes which are considered as nano factories possess a host of reductase enzymes that help to detoxify heavy metals also play a significant role in the reduction of metal salts into nanoparticles. Niknejad et al reported synthesis of Ag-nanoparticles by growing yeast cells in a suspension of $AgNO_3$, possibly by the help of an or sulphate reductase system with ATP as the energy source and NADH as the cofactor for reduction [15]. The mono-dispersed spherical Ag-Nps demonstrated high antifungal activity against a wide variety of *Candida* sp strains known as "opportunistic pathogens" [16]. Another study showed that the "oily yeast" *Yarrowia lipolytica* synthesized pyomelanin that was utilized for synthesis of nanocrystalline Au-NPs [17]. Ahmed et al. reported synthesis of Se nanoparticle from *Stenotrophomonas acidaminiphila* which is widely used as an agricultural sensor to detect heavy metal toxicity. Although the mechanism is not very well explained, it is assumed that the reaction is catalyzed in-vivo by a NADPH-dependent reductase. Plant-mediated nanoparticle biosynthesis involves a single step that has drawn attention recently because of its rapid, eco-friendly, nonpathogenic, and low-cost method. The reduction occurs by combining biomolecules (such as amino acids, polysaccharides, terpenes, alkaloids, phenolics etc.) that act as reducing agents and phytoconstituents as the capping agents. Naseer et al. reported that leaf extracts of *Cassia fistula* and *Melia azadarach* enabled the synthesis of ZnO nanoparticles [18]. Similarly, [19] and [20] reported that root extract of *Asparagus racemosus* and leaf and seed extract of *Aloe vera* and flax seeds could be used to synthesize spherical palladium and iron oxide nanoparticles which have varied applications. The biogenic process which has the advantages of non-toxicity, reproducibility in production, easy scaling-up with low energy requirements eliminates the use of expensive chemicals lowering the production cost and is environment-friendly. Moreover, particles generated by this process have greater specific surface area, higher catalytic reactivity and facilitates improved contact between the enzyme and metal salt which is estimated to be a common trend in nanoparticle production in the coming years. However, the green synthesis of nanoparticles has its limitations. Although this method can help reduce pollution, it may also be economically challenging due to the cost of certain natural precursors and the potential need for additional processing [21, 22]. Additionally, extraction and purification can be complicated by the presence of unwanted biocompounds [23]. These issues can hinder the broader adoption and development of green-synthesized nanoparticles in the nanotechnology industry.

4. Applications of nanoparticles: A host of endless opportunities

Nanoparticles have promised a wide range of applications (Figure 1) in various dimensions spanning health care, diagnostics, bioenergy, agriculture, catalysis, and most importantly, the environment (summarized below).

4.1 As manufacturing material

Nanoparticles provide unique materials for material science with special mechanical, optical and electrical properties with varied applications in medical and commercial sectors. The health fitness products occupies a lion's share of the nanotechnology consumer product's category followed by electronics and computer parts. It has also revolutionized the food and packaging industry. The absorption features of noble non-metals Ag and Au have been exploited for a wide variety of applications including chemical sensors and biosensors. In case of food safety analysis, with the help of an “electronic tongue” or “nose” nanoparticles can detect toxins, adulterants, pathogens, sugar, and antioxidants [24]. Industries related to cosmetics are using nano scaled materials for deeper skin penetration, UV protection, antibacterial properties and in toothpaste formulas [25].

Table 1 The physical and chemical methods of NP synthesis using top down and bottom up approaches.

SL No	Approach	Method name	Principle	Application	Remarks	Reference
1.	Top down	Mechanical milling	Attrition based method where kinetic energy is transferred from medium to the grinding material.	Production of nano-composites. Wire resistant spray coatings. Environmental remediation, energy storage and conversion.	Cost-effective method. Produces blends of different phases.	[26]
2.		Electrospinning	Application of high voltage electric field aiming to extract very thin fibres from a polymeric fluid stream	Production of ultrathin nano-fibers. Development of core–shell and hollow polymer, and hybrid materials.	Simple method of synthesis.	[27]
3.		Sputtering	Bombardment of solid surfaces with high-energy particles such as plasma or gas	Used in production of thin film nanomaterials. Used in several industries such as microelectronics, optical coating, semiconductors.	Sputtered nanomaterial composition remains the same as the target material with very few impurities.	[28]
4.		Laser ablation	Nanoparticle generation using a powerful laser beam that hits the target material	Production of monodisperse colloidal nanoparticle solutions. In synthesis of carbon nanomaterials, oxide composites and ceramics.	Green technique, as there is no need for stabilizing agents or other chemicals.	[29]
5.	Bottom up	Chemical vapour deposition (CVD)	In this process, the substrate is exposed to one or more volatile precursors, which react and/or decompose on the substrate surface to produce the nanomaterial deposit.	Conductive plugs onto semiconductor devices. Graphene synthesis. Synthetic diamonds.	Excellent method for producing high-quality 2D nanomaterials.	[30]
6.		Hydrothermal (HT) &Solvothermal (ST) method	In these methods, nano-structured materials are attained through a heterogeneous reaction carried out in a liquid medium at high pressure and temperature around the critical point in a sealed vessel. For, ST method the medium is essentially non-aqueous a non-aqueous medium	Used in the production of nanowires, nanorods, nanosheets, and nanospheres.	Most well-known and extensively used method.	[31]
7.		Sol-gel method	The process involves hydrolysis of metal oxides in water with the assistance of alcohol to form a sol. The next step involves condensation increasing the solvent viscosity to form porous structures left to age. This is followed by drying and calcination to achieve nanoparticles.	Used for the development of various kinds of high-quality metal-oxide-based nanomaterials.	Wet chemical technique. Economically friendly.	[32]
8.		Reverse micelle method	This method with reversed micellar templates, allows different reactants solubilized in separate micellar solutions to react upon mixing. The micelles act as "nanoreactors" providing a suitable environment for controlled nucleation and growth. Additionally, the steric stabilization provided by the surfactant layer prevents the nanoparticles from aggregating.	Production of nanorods. Fuel cell synthesis.	The size of nanomaterials can be controlled. Nanoparticles developed are amazingly fine and monodispersed in nature.	[33]

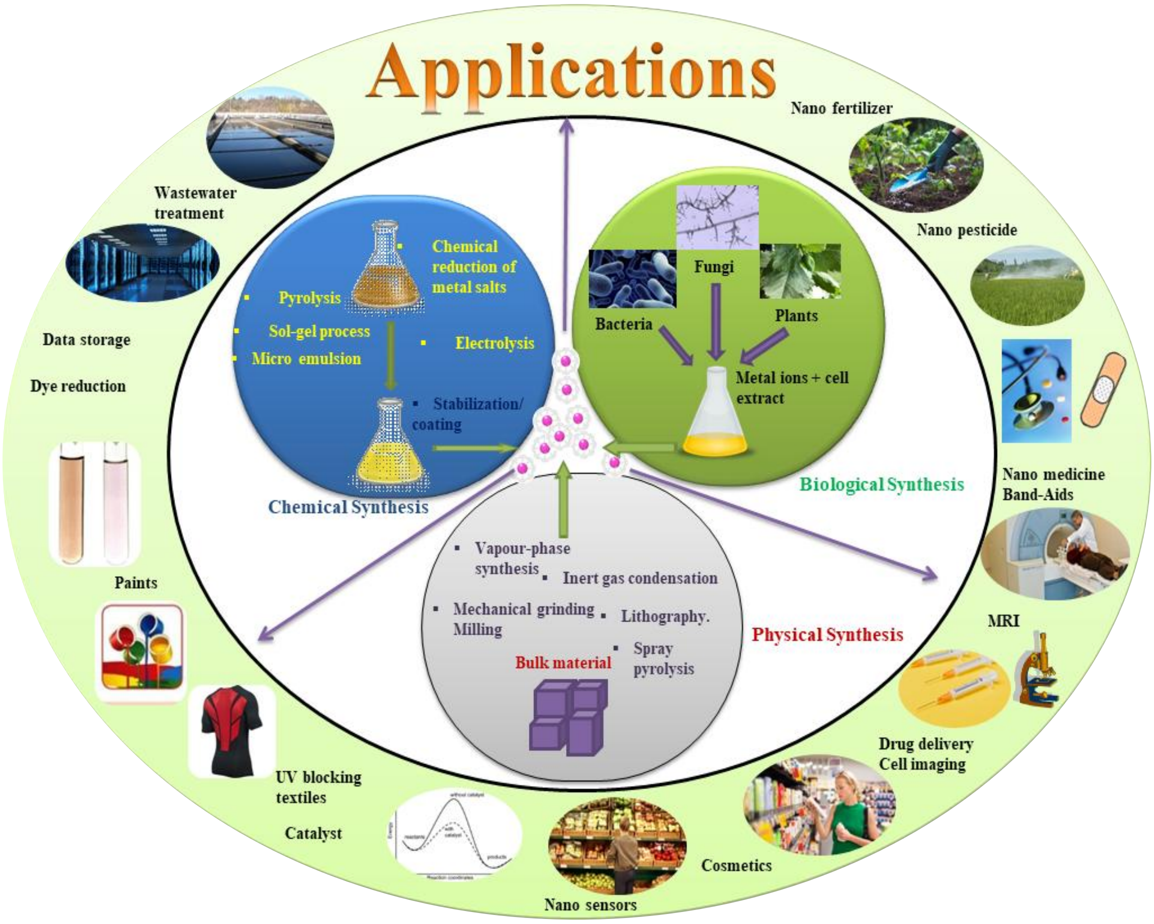

Figure 1 An illustration of synthesis as well as several applications of nanoparticles.

4.2 Biomedical applications

NP's have attracted interest from different branches of medicine for their ability to deliver drugs in optimum range that significantly enables therapeutic drug efficiency with reduced side effects. Drugs with poor solubility and absorption ability are currently tagged with nanoparticles [34]. Also, for photo thermal and contrast based imaging applications, the optical properties of NPs have been significantly exploited. The Iron Oxide particles are the most commonly employed for different biomedical applications. Superparamagnetic iron oxide NPs with appropriate surface chemistry have been used in numerous in vivo applications such as MRI contrast enhancement, tissue repair, immunoassay, detoxification of biological fluids hyperthermia, drug delivery, and cell separation. Polyethylene oxide and polylactic acid NPs have been extensively used for intravenous drug administration. For selective photo thermal therapy of cancer, metallic nanoparticles have shown significant promise. The antineoplastic effect of the NP's has been effective in inhibiting tumour growth. Due to their different antimicrobial properties, Ag Nps are extremely popular as a catheter material, used in wound care issues and also a component of various medical utensils [35]. Green synthesized Au NP's also exhibited dose-dependent antibacterial potential against *K. pneumonia, P. aeroginosa*, and *E coli* [36]. The antimicrobial characteristics of inorganic NPs make them a suitable alternative to the organic inhibitors, which are relatively toxic to the biological system.

4.3 Sustainable agriculture

Literature studies have evidenced that interaction and uptake of nanomaterials lead to changes in the plant at a molecular level and significantly affect the overall plant physiology. Crops such as barley, soybean, and corn have shown enhanced growth when exposed to carbon nanomaterials. Also, the advanced seed priming technique widely used with the application of nanotechnology now a day's enables rapid and uniform seed germination and seedling emergence [37]. Also, NP's have shown to promote response to abiotic stress in plants such as drought, salinity, temperature fluctuations and mineral toxicity. Toxic metals get adhered to the large surface area of nanoparticles thereby reducing its availability. Also, Np's act in a fashion similar to antioxidant enzymes that reduce oxidative stress [38]. Avestan et al., reported application of silicon dioxide-nanoparticles on salt stress improvement of strawberry plants which are very sensitive to salinity. The plants treated with silicon dioxide nanoparticles (0, 50, 100 mg/l) showed potential ability in maintaining epicuticular wax structure, chlorophyll and carotenoid content, supressing the adverse effects of high salt concentration [39]. Nanoparticles have also showed potential as pesticide delivery carriers [40]. Among different types of NPs, the solid and mesoporous silica NPs have shown the most potential delivery agent of agrochemicals due to their structural flexibilities [41].

4.4 Energy storage and generation

The transition from non-renewable fossil fuel to renewable energy sources (as a part of different government directives) to mitigate global warming has prompted the scientific world to look for alternative sources for energy generation and storage at cheaper cost [42]. The large surface area, optical properties and catalytic nature of the NPs make them most suitable for this purpose. NP's have been widely used to generate energy from electrochemical water splitting. Also, electrochemical CO_2 transformation to its fuel precursors, solar cells also have demonstrated options to produce energy [43]. Unconventional approaches such as nano-generators have been created which are capable of transforming mechanical, energy into electrical energy and subsequent storage [44].

4.5 As a mechanical agent

Nanoparticles have excellent mechanical properties that can be used in different mechanical industries in coating, lubricant and adhesive applications. Nanoparticles added to a common material, significantly improve the grain boundary and promote the mechanical properties of materials. [45] demonstrated that 3 wt/% nano-SiO_2 to concrete improved its compressive strength, bending strength, and splitting tensile strength. In addition, NPs offer good sliding and delamination properties, which also promote low friction and wear, and hence increased lubrication effect [46].

5. Accumulation of nanoparticles in the environment: a potential threat

As nanoparticles are increasingly produced and used, they inevitably find their way into the environment during their use and disposal. Nanoparticles from various sources can have diverse and significant impacts on human health, plants, animals, and ecosystems, with the extent of these effects largely determined by their physical and chemical properties, exposure routes, and the biological systems they encounter. Soil and water are primary reservoirs where nanoparticles can accumulate in significant quantities [5, 47]. Their presence can alter soil chemistry, affect microbial communities, and disrupt aquatic ecosystems. For instance, nanoparticles can impact nutrient cycling and microbial respiration in sediments, both of which are crucial for ecosystem health [48]. They may also be taken up by plants through their roots [5]. Current research in agriculture and nanotechnology is focused on developing nano-pesticides and nano-fertilizers [40, 49]. While these innovations can boost crop yields, excessive use of such "nano-agrochemicals" may lead to soil bioaccumulation problems. Nanoparticles in the soil undergo transformations that facilitate their accumulation [50]. They interact with plant roots, translocate to aerial parts, and accumulate in cellular organelles [51]. For example, silver nanoparticles can inhibit plant growth and development by disrupting essential physiological processes such as photosynthesis, nutrient uptake, water transport, and hormonal regulation. These disruptions can adversely affect productivity and the quality of harvested crops, posing risks to agricultural productivity and ecosystem stability [52]. Similarly, nanoparticles accumulate in aquatic environments (lakes, rivers, estuaries, and seawater) through industrial and domestic wastewater discharges [53]. Nanoparticles from cosmetics, paints, and biomedical waste contribute significantly to this accumulation. In aquatic organisms, these particles can penetrate through the gut, gills, and other internal organs. In humans, nanoparticles can enter the body through inhalation, ingestion of contaminated water, injection, or skin contact, as well as indirectly through consumption of vegetables, fish, molluscs, and crustaceans [53, 54]. Inhaled nanoparticles can bypass the body's defense mechanisms and cause systemic health issues by dispersing to various organs [55]. Long-term exposure has been linked to reproductive and developmental problems in animals, as well as changes in behaviour and immune responses.

5.1 Physicochemical properties of NPs and their mechanism for cellular internalization and toxicity

The cellular internalization mechanisms and toxicity profiles of nanoparticles (NPs) vary divers depending upon their physicochemical properties. Toxicity of the nanoparticles here refers to the ability of the particles that impacts the structure & physiology of the organ or tissue of any organism, including humans and animals [56]. Upon reaching the cell's exterior membrane, nanoparticles (NPs) interact with the components of the plasma membrane or extracellular matrix, subsequently entering the cell predominantly via endocytosis [57, 58]. This process involves the invagination of the membrane, leading to the encapsulation of NPs within forming endocytic vesicles. These vesicles then detach from the membrane and are directed to specialized intracellular compartments responsible for sorting and trafficking [57].

Numerous researchers have tried studying the cytotoxicity of the nanoparticles, both *in vivo* and *in vitro* approaches. Though many aspects of nanoparticle toxicity are still under research, their surface charge and the fact that some nanoparticles are "redox-active" and particles can "penetrate" the cell membrane are of main toxicological concern (Figure 2) [59]. Studies show that nanoparticles of smaller size (<10 nm) can act similar to the gas that can penetrate the cells and damage the cell organelles (Figure 3) [60]; hence it contributes to higher toxicity compared to larger-sized particles. Nanoparticles possess higher chemical reactivity due to the higher surface-to-volume ratio. This higher chemical reactivity results in

the increased production of reactive oxygen species which, when in contact with biomolecules, causes oxidative stress, protein damage, DNA damage & inflammation [61].
The shape or crystallinity of a nanoparticle can also influence its toxicity [62]. For instance, rod-shaped nanoparticles may be more toxic than spherical one of the same material due to their higher aspect ratio, which can increase their ability to interact with cells and cause damage [63]. Similarly, the surface coating of NPs can affect their toxicity by altering their interactions with biological systems [62]. For example, NPs with a hydrophilic coating may be less toxic than those with a hydrophobic coating, as they are less likely to interact with and damage cell membranes [63].

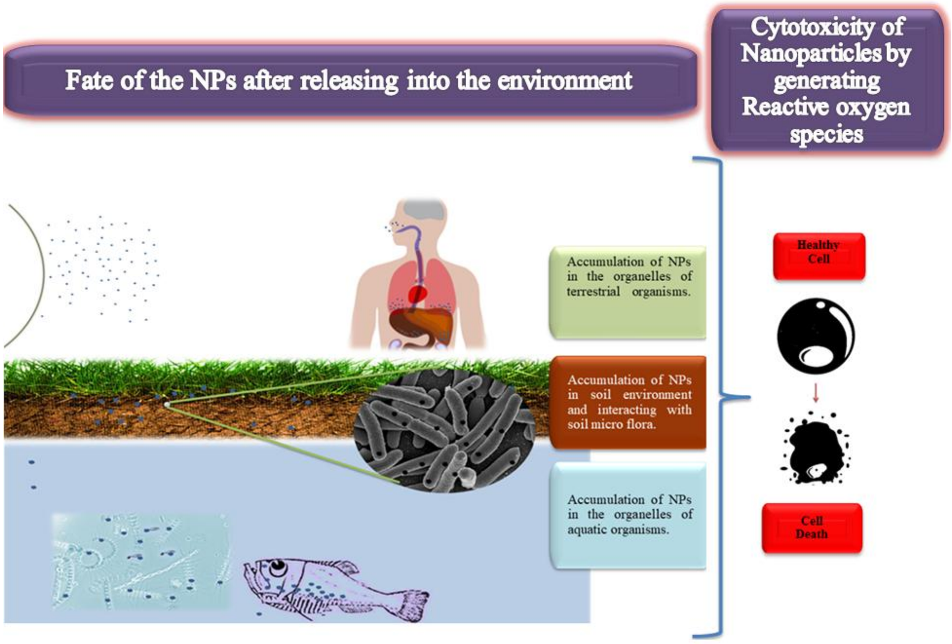

Figure 2 An illustration of the fate and toxicity of the nanoparticles after releasing into the environment.

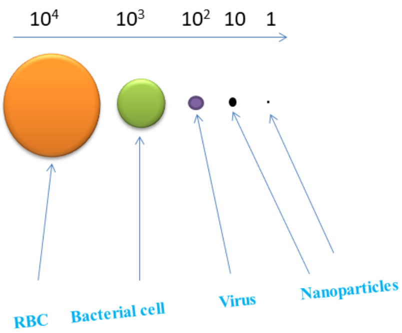

Figure 3 Size comparison (nm) of nanoparticles with larger sized cells.

Literature results illustrate that oral administration of TiO_2 to the three-week-old healthy Sprague-Dawley rats at 2, 10, 50 mg/kg for a period of 30 to 90 days significantly harmed the cardiovascular system, causing arrhythmia, lowering of systolic blood pressure, and an increase in diastolic blood pressure [64]. Many researchers have observed that upon oral administration of the nanoparticles, they translocate further to the other body organs and interfere with the normal physiology [65, 66]. For instance, after the oral administration of different-sized silver nanoparticles to the rat, [65] found silver accumulation in the body's other organs, including the brain, lung, liver, kidney & testis. Further, it was also revealed that repeated oral administration with 1 mg/kg of small-sized (22nm) silver nanoparticles in rats resulted in a significant increase in the level of pro-inflammatory cytokines (IL-1, TNF-, and IL-6) Th1 type cytokines (IL-12 and IFN), Th2-type cytokines (IL-4, IL-5, IL-10), CD8+ T cell distribution & TGF-β, which is responsible for regulating crucial cellular activities and its increase may lead to cancer [65]. An NMR-based metabolomic study exposure of TiO_2 nanoparticles to the zebrafish has revealed its nanotoxicity on its metabolism. The exposure of TiO_2 nanoparticles induced a rise in the level of xanthine, an irreversible product of the purine salvage pathway. An increase in the xanthine level caused an interruption between energy and purine metabolism [66]. Similarly, toxicity and distribution of other nanoparticles, including Au, ZnO_2, SiO_2& TiO_2 have also been studied by various researchers and it has been documented that prolonged exposure of the nanoparticle may cause harm to the individual [67-70]. Though soil and water are the main source for nanoparticle accumulation, nanoparticles may become airborne during manufacture, packaging and application [71]. Hence, one cannot deny that nanoparticles may interact with the human lung tissue as it is the receptor of the air. [72] studied the toxic effects of silver nanoparticles to the female Wistar rat lung by using Quantitative laser-ablation inductively-coupled plasma mass spectrometry (LA-ICP-MS) combined with enhanced dark field microscopy and autometallography It was found that 75-150μg of NPs caused mild inflammation in the lungs characterized by increased amount of polymorpho-nuclear-neutrophilic granulocytes and alveolar macrophages in broncho-alveolar lavage fluid (BALF), accompanied by elevated protein concentrations and 300μg amount of NPs caused genotoxicity. Moreover, the study further revealed that the silver nanoparticles from lung, localized to the peripheral organs, including liver, kidney and spleen [72]. In another study by Hallock et al, nanoparticles were also found to translocate to the olfactory lobe, cerebellum and cerebrum part of the brain through nasal mucosa along the olfactory nerve [73]. The effect of nanoparticles on various organs has been summarized in the Table 2.

We understand that the impact on ecotoxicity and human health of the nanomaterials dramatically depends on its size, thickness, surface functionalization. Although preliminary studies have revealed certain adverse effects, extensive chronic toxicity analysis is needed to improve the robustness and accuracy of effect factors (which are taken into account for the toxicity analysis) since size of the nanomaterials make it particularly challenging to perform accurate predictions [74].

5.2 Physicochemical properties of NPs and their mechanism for cellular internalization and toxicity

The growing demand that has catalyzed the development of large-scale nano-enabled products over the past decade has also raised concerns regarding the establishment of safe technologies from an environmental viewpoint. With the current environmental norms, impact assessment (IA) of products and processes is a must, with government policies focused on mitigating non-renewable energy usage and material consumption. From an industrial perspective, safety aspects, end-of-life analysis, and resource consumption from the R&D onset are essential, enabling early decision-making for environmentally benign processes and products. Although EIA studies on nanotechnology haven't been studied in great detail, few researchers have utilized LCA and RA to analyze the impact [75, 76].

An extensive literature search revealed that most of the studies published have considered only cradle-to-gate life cycle analysis with the functional unit in terms of weight of the synthesized nanoparticle (either 1 g of 1 kg of the nanomaterial). The studies have primarily focused on environmental impacts in terms of midpoint indicators such as climate change, eutrophication, and ozone layer depletion (ODP), while only a handful of research considered endpoint analysis on human health [77]. [77] reported that use of nanomaterials primarily result in greenhouse gas (GHG) emissions (~3.0 kg CO_2eq per functional unit) and impact acidification (10-20 kg SO_2eq per functional unit) of terrestrial, aquatic systems and affects eco-toxicity (~8-10 CTUe/kg). Sackey et al. [78] on the other hand reported that by using a mixture of nanomaterials (nano-silica-asphalt) instead of conventional material (asphalt), GHG emissions and other impact categories could be substantially reduced. Certain researchers have additionally considered the fate factor and the exposure factor of the nanomaterials when evaluating their effects on the environment [79]. However, most of these studies have considered worst-case scenarios with the highest possible exposure, although the value of the fate and exposure factor varies greatly from one system to another depending on the point of release and its transport mechanism.

There is almost no report on the generation and management of nano-waste, one of the most crucial aspects of LCA studies on nanomaterials. We could find only a single study that reported impact assessments up to the disposal (end of life) of nanomaterials for coating systems containing nano TiO_2. The report revealed substantial improvement in the coated nanomaterials' environmental performances compared with conventional coating systems [80]. However, the study also emphasized ways to recycle or reuse the material must be established to reduce landfilling to the lowest possible level.

However, it is unfair to mention that all the environmental impacts occur from the synthesis and use of nanomaterials since indirect emissions from background systems, such as transport and production of heat and electricity, also contribute to a significant degree in the overall emission statistics. Also, there are significant uncertainties to the predicted environmental impacts for the EIA since once released into the environment, nanomaterials undergo a lot of transformation, and their persistence in the environment varies greatly, which cannot be accurately predicted with existing models (on nanomaterials) owing to limited availability of datasets.

6. Approaches to attenuate toxic effects of NPs

Owing to the widespread use of nanoparticles (NPs) and their potential negative biological impacts, research is increasingly focused on developing strategies to minimize NP toxicity and remove them from the environment. One commonly employed method involves altering the surface chemistry and properties of NPs, as surface characteristics play a crucial role in determining their toxicity [81]. By modifying the dispersion state of nanoparticles through surface coating, their bioavailability and potential hazardous effects can be influenced. For instance, coating NPs with materials like polyethylene glycol (PEG) or zwitter-ionic polymers can improve biocompatibility, alter dispersion, and reduce toxicity by shielding reactive surface sites [81]. A novel approach involves coating NPs with naturally derived cell membranes, such as those from red or white blood cells. This technique facilitates long-term circulation and targeted recognition of specific sites [82]. Additionally, environmentally friendly synthesis methods, such as those utilizing plant extracts or microorganisms, can produce less toxic NPs by employing natural stabilizers that are less harmful than synthetic chemicals.

Table 2 Effect of nanoparticles on various animal organs based on *in vitro* and *in vivo* studies.

Cells/Organ for study	Nanoparticles	Dosage	Effect	Assessment method	Reference
Neurobehavioral study	Silver (20 nm)	0.8-1.5 mg/kg	Anxiety like behaviour and severe ultra-structural changes in neurons	Open field test and elevated plus maze	[83]
Human Lung epithelial cells A549	Silica (20 nm)	8, 16, 32, 64 &128 μg/mL	ABC transporters inhibition	Calcein-AM assay	[84]
Lung cells	Citrate coated Silver (20 & 110 nm)	0.1 mg/kg	Characteristics of asthma-like bronchial hyper responsiveness and eosinophilic inflammation	*In vivo* animal model studies	[85]
Reproduction system	Nickel (90nm)	15-45 mg/kg	Decrease in ovarian weight & inflammation	*In vivo* animal model studies	[86]
Liver cells	Zinc oxide	300 mg/kg	DNA damage along with altering various enzymes	Comet assay	[87]
Human Mesenchymal stem cells	Aluminium oxide (160 nm)	25-40 µl/mL	Cytotoxicity	MTT assay	[88]

To protect the aqueous environment from nanoparticle accumulation, it is essential to monitor the availability of the nanoparticles in the water resources to get an idea of the intensity of its impact on the environment. In recent years it has become possible to detect and measure the concentration of NPs. [89] studied and developed a rapid (SP-ICP-MS) analytical method to measure and quantify several nanoparticles, including titanium dioxide, silver, and gold. The presence of nanoparticles has been studied in various water resources, including the Texas River, Trinity River estuary & Rhine River [90]. Once nanoparticles accumulate in a particular environment, they may react with other molecules and transform into other forms. Different reactions, including redox, dissolutions, and aggregations, lead to the transformation of nanoparticles. It is crucial to understand these transformations as it decides the toxicity & fate of the nanoparticles in the environment [91]. Understanding the toxicity mechanism of the nanoparticles may help in the synthesis of neutral nanoproducts that will not cause harm directly to the organism. However, the potential toxicity of the nanoparticles is still under research. Since Nanoproducts are being manufactured on a large scale; one thing that cannot be avoided is the release of those products and their by-products into the aquatic environment through industrial and domestic waste-water, followed by the transformation of the nanoparticles by interacting with other molecules present in the aquatic environment that decides their fate and toxicity [92]. A large amount of nanoparticles in the wastewater may adsorb to the biomass in the water and can be removed along with sludge [47] however, the remaining amount of the particles will still be in the water. Moreover, the fate of most of the removed sludge is landfilling, which again leaves the nanoparticles in the environment only. Hence, from this standpoint, removal & recovery of the nanoparticles from waste water & prevent them from reaching to the environment is the need of the hour.

6.1 Techniques being used in nanoparticles separation

Removal of nanoparticles is not only necessary but also a challenging task since the small size and unique surface properties of nanoparticles makes the separation process difficult by traditional methods like filtration and centrifugation. Limbach et al. studied the removal of oxide nanoparticles, especially cerium oxide. It was observed that these oxide particles could react with the sludge in the waste-water, which helps stabilize the surface charge resulting in the formation of agglomerates that can be easily separated from wastewater [93]. Though activated sludge can remove around 90% of the nanoparticles from waste water, the remaining amount in the water may also be of concern [94]. Some techniques including coagulation, flocculation, aggregation, adsorption, floatation, etc., have been used so far by various researchers for the removal of nanoparticles (Table 3). Liu et al. studied the separation of silica nanoparticles from water by aggregation process.$AlCl_3$was selected as the additive to destabilize nano-SiO_2 suspensions for the separation proposed [53]. However, the results illustrated thatthe nanoparticle removal is considerably slow, making the process time consuming (≈ 2 weeks) and not feasible for large-scale application. Also, the technique leaves traces of aluminum salt in the treated water, making it unsafe for human consumption as it may potentially lead to Alzheimer's [95]. Many researchers have applied a combination of a flocculation-coagulation process for the separation of fine particles from water by using either commercially available coagulants (aluminum sulfates, iron sulfates, and aluminum chloride) or natural coagulants (gelatin, plant seeds) [96].

Table 3 Techniques for the removal of nanoparticles from wastewater.

Techniques	Reagent/ material used for separation	Loading amount	NPs separated	%age removal	Remarks	References
Coagulation, flocculation and sedimentation	Polyalluminium chloride	5 & 30 mg/L	TiO_2, Ag &CuO	100	The differences between water characteristics including turbidity and organic matter content play an important role on the coagulant demand.	[97]
Flocculation-floatation	Iron hydroxide and gelatinized corn starch.	Fe $(OH)_3$: 40 mg/L Corn starch: 15 mg/L	TiO_2	95-100	Combination of Fe $(OH)_3$ (a coagulant) and gelatinized corn starch (a flocculant) yielded dense flocs which allowed rapid and effective separation of TiO2- NPs.	[98]
Flocculation-coagulation	polyaluminum ferric chloride, cationic polyacrylamide, & Kaolin	30 mg/L	TiO_2	98.62	The removal of TiO2-NPs was enhanced by kaolin. The inorganic coagulant PAFC and the organic flocculent CPAM were used together to improve the compactness and stability of the flocculant.	[99]
Coagulation	aluminium sulphate, ferric chloride, poly aluminum chloride & polyferric sulphate	495 mg/L	Silver	99	Effective coagulation was achieved at optimum pH 7.5	[100]
Adsorption	PVA/gluten hybrid nanofibers	0.5 g/L	Gold & Silver	99	The PVA/gluten hybrid nanoparticles are able to adsorb the negatively charged nanoparticles by electrostatic interaction.	[101]
Aggregation	Aluminium chloride	100 mmol/l	Silica	>99	Addition of $AlCl_3$ modifies the surface properties of the nanoparticles leads to the aggregation of the particles	[53]
Magnetic seeding aggregation	Magnetite nanoparticles	10 g/L	Silica	Not mentioned	Turbidity of waste water reduced effectively due to electrostatic attraction between magnetic nanoparticles and silica nanoparticles	[102]

Interestingly, some researchers suggest that plants have an interesting coagulant activity due to the presence of its constituents such as starch, cellulose, lignin, hemicellulose and pectin that can be utilized for separation purposes. Shilpa et al. studied the flocculation-coagulation activity of Hyacinth bean peels and *Opuntia ficusindica* against suspended particles and removed 89.03% and 77.10%turbidity, respectively [95]. However, it is not studied whether nanoparticles can be removed by this process or not. [99] studied flocculation-coagulation of nanoparticles for efficient removal by using poly aluminum ferric chloride (PAFC) & cationic polyacrylamide (CPAM). [103] used bio sorption technique to remove TiO_2, Fullerene and silver nanoparticles from waste-water. In this technique, an increased amount of natural organic material and exopolysaccharide in the biomass could efficiently remove the nanoparticles from water. To neutralize the surface properties, the floatation technique can also be used [47]. Although the processes mentioned above can effectively remove nanoparticles in water, these processes also have many shortcomings, including high cost, poor efficiency at high concentrations of nanoparticles, and time-consuming [98].

7. Conclusion

Nanotechnology has made tremendous progress in history with rapid expansion in different industrial sectors. The world has witnessed a steady rise in the synthesis and application of varied nanoparticles making it a billion dollar industry with a CAGR of ~10%. Although termed a "host of endless opportunities" due to their multifaceted applications, the nanoparticles as a flip side of the coin have certain negative aspects in terms of their environmental concerns. The use of harsh chemicals and techniques employed in the synthesis of these NP's have recently created a stir amongst the research fraternity to shift towards greener synthesis routes that cause lower environmental impacts. With persistent use, nanoparticle accumulation in the environment may severely affect the air, soil and water bodies with potent threat to marine and terrestrial species. To address the issue, methods are being developed (across the globe) which alone or in combination can selectively remove the particles to prevent it's accumulation with efficient recycling. However, scalability and economic viability still remains a challenge for these processes which would require significant technical advancements to make them a commercial success for environmental remediation.

Author Contributions

AAS and DDG Wrote the Original Draft. AAS and DDG Edited the Draft. DDG and SVM Reviewed and finalized the Manuscript.

Data Availability Statement

This is a review article and does not contain any research data.

Competing Interests

Authors do not have any conflicts of Interest.

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